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(54) **Separation of organic oxygenates.**

(57) Concentration of solutions containing methanol and either dimethyl carbonate or methyl t-butyl ether may be effected by a composite membrane including a dibromobutane cross-linked poly(4-vinyl pyridine) bonded to a porous layer of polyacrylonitrile on a polyester backing.

EP 0 584 411 A1

This invention relates to the separation of organic oxygenates such as methyl alcohol. More particularly it relates to a membrane technique for effecting separation of methanol and/or ethanol from reaction mixtures containing methanol and/or ethanol together with products such as methyl t-butyl ether or dimethyl carbonate.

It is known in the art that it is possible to separate mixtures of liquids by various techniques including adsorption or distillation. These conventional processes, particularly distillation, are however, characterized by high capital cost. In the case of distillation for example the process requires expensive distillation towers, heaters, heat exchangers (reboilers, condensers, etc.), together with a substantial amount of auxiliary equipment typified by pumps, collection vessels, vacuum generating equipment.

Such operations are characterized by high operating costs, principally costs of heating, cooling and pumping.

Furthermore the properties of the materials being separated, as is evidenced by the distillation curves, may be such that a large number of plates may be required. When the material forms an azeotrope with water, additional problems may be present which for example, would require that separation be effected in a series of steps (e.g. as in two towers) or by addition of extraneous materials to the system.

There are also comparable problems which are unique to adsorption systems.

It has been found to be possible to utilize membrane systems to separate mixtures of miscible liquids by pervaporation. In this process, the charge liquid is brought into contact with a membrane film; and one component of the charge liquid preferentially permeates the membrane. The permeate is then removed as a vapor from the downstream side of the film - typically by sweeping with a carrier gas or by reducing the pressure below the saturated vapor pressure of the permeating species.

Illustrative membranes which have been employed in prior art techniques include those set forth in the following table:

#### TABLE

##### Separating Layer

- Nafion brand of  
perfluorosulfonic acid

- Sulfonated polyethylene

- Fluorinated polyether  
or Carboxylic Acid fluorides

##### References

- Cabasso and Liu  
J. Memb. Sci. 24,  
101 (1985)

- Cabasso, Korngold  
& Liu J. Pol. Sc:  
Letters, 23, 57  
(1985)

US-A-4,526,948  
to Dupont as assignee  
of Resnickto

TABLESeparating Layer

5 - Selemion AMV  
brand of Asahi Glass  
cross-linked styrene  
10 butadiene (with quaternary  
ammonium residues on a  
polyvinyl chloride backing)

15 - Cellulose triacetate

20 - Polyacrylonitrile

25 - Crosslinked  
30 Polyvinyl Alcohol

35 - Poly(maleimide-  
acrylonitrile)

40 - Dextrine -  
isophorone diisocyanate

References

- Wentzlaff  
Boddeker & Hattanbach  
J. Memb. Sci. 22,333  
(1985)
- Wentzlaff, Boddeker  
& Hattanback, J. Memb.  
Sci. 22, 333 (1985)
- Neel, Aptel &  
Clement Desalination  
53, 297 (1985)
- EP-A-0096339 (GFT)
- Yoshikawa et al  
J. Pol. Sci. 22, 2159  
(1984)
- Chem. Econ. Eng.  
Rev., 17, 34 (1985)

45 The cost effectiveness of a membrane is determined by the selectivity and productivity. Of the  
membranes commercially available, an illustrative polyvinyl alcohol membrane of high performance is that  
disclosed in EP-A-0096339 (GFT). EP-A-0096339 discloses, as cross-linking agents, diacids (typified by  
maleic acid or fumaric acid); dihalogen compounds (typified by dichloroacetone or 1,3-dichloroisopropanol);  
aldehydes, including dialdehydes, typified by formaldehyde. These membranes are said to be particularly  
50 effective for dehydration of aqueous solutions of ethanol or isopropanol.

This reference discloses separation of water from alcohols, ethers, ketones, aldehydes, or acids by use  
of composite membranes. Specifically the composite includes (i) a backing typically about 120 microns in  
thickness, on which is positioned (ii) a microporous support layer of a polysulfone or a polyacrylonitrile of  
about 50 microns thickness, on which is positioned (iii) a separating layer of cross-linked polyvinyl alcohol  
55 about 2 microns in thickness.

Polyvinyl alcohol may be cross-linked by use of difunctional agents which react with the hydroxyl group  
of the polyvinyl alcohol. Typical cross-linking agent may include dialdehydes (which yield acetal linkages),  
diacids or diacid halides (which yield ester linkages), dihalogen compounds or epichlorhydrin (which yield

ether linkages) olefinic aldehydes (which yield ether/acetal linkages), boric acid (which yields boric ester linkages), sulfonamidoaldehydes, etc.

See also J. G. Prichard, Polyvinyl Alcohol, Basic Properties and Uses, Gordon and Breach Science Publishers, New York (1970) or

5 C. A. Finch, Polyvinyl Alcohol, Properties and applications, John Wiley and Sons, New York (1973) or US-A-4,798,674 to Pasternak, Bartels, and Reale.

US-A-4,728,429 (Cabasso et al), US-A-4,067,805 (Chiang et al), US-A-4,690,766 (Linder et al) provide additional background.

Additional prior art includes:

10 Effect of Quaternization on the Pervaporation Rate of Water Through Poly(4-Vinylpyridine) Membrane, Hamaya, and Yamada, in Kobunshi Ronbunshu, 34(7), 545-7, 1977.

Preparation of Separation Membranes, Yamamoto, Toi, and Mishima, patent #JP 61/161109 A2, Jul 21 1986. (Japanese).

15 Separation of Some Aqueous Amine Solutions by Pervaporation through Poly(4-Vinylpyridine) Membrane Yamada and Hamaya, in Kobunshi Ronbunshu, 39(6), 407-14, 1982.

Complex Formation of Crosslinked Poly(4-Vinylpyridine) Resins with Copper (II), by Nishide, Deguchi, and Tsuchida, in Bulletin of the Chemical Society of Japan, Vol. 49(12), 3498-3501 (1976).

EP-A-0425108 (Texaco) describes the concentration of charge aqueous solutions of an organic oxygenate utilising a membrane of poly(vinyl pyridine) cross-linked with an aliphatic polyhalide.

20 EP-A-0480599 (Texaco) describes a non-porous membrane comprising a separating layer of poly(vinyl pyridine) which has been cross-linked with an aliphatic polyhalide.

It is an object of this invention to provide a novel separation process for organic oxygenates.

In accordance with certain of its aspects, this invention relates to a method of concentrating a charge solution containing (i) an alcohol having less than three carbon atoms and (ii) an organic oxygenate selected from organic ethers, aldehydes, ketones, esters, and mixtures thereof which comprises:

25 passing the charge solution into contact with a first (high pressure) side of a non-porous separating layer, a pressure drop being maintained across said layer, whereby at least a portion of said alcohol and a lesser portion of organic oxygenate from said charge solution pass by pervaporation through said non-porous separating layer to a second (low pressure) side thereof thereby providing a permeate on the low pressure side comprising a lean mixture containing more alcohol and less organic oxygenate than are present in said charge solution, said lean mixture being recovered in vapor phase at a pressure below the vapor pressure thereof; and a retentate on the high pressure side comprising a lower alcohol content and a higher organic oxygenate content than are present in said charge solution, characterised in that said non-porous layer is a membrane of a poly(vinyl pyridine), cross-linked with an aliphatic polyhalide.

35 The invention further relates to the use of a membrane comprising poly(vinyl pyridine) which has been cross-linked with an aliphatic polyhalide in concentrating a charge solution containing (i) an alcohol having less than three carbon atoms and (ii) an organic oxygenate selected from organic ethers, aldehydes, ketones, esters, and mixtures thereof.

40 The composite structure of this invention includes a multi-layer assembly which in the preferred embodiment preferably includes a porous carrier layer which provides mechanical strength and support to the assembly.

#### THE CARRIER LAYER

45 This carrier layer, when used, is characterized by its high degree of porosity and mechanical strength. It may be fibrous or non-fibrous, woven or non-woven. In the preferred embodiment, the carrier layer may be a porous, flexible, non-woven or woven fibrous polyester.

50 A preferred non-woven polyester carrier layer may be formulated of non-woven, thermally-bonded strands and characterised by a fabric weight of  $80 \pm$  grams per square yard ( $96 \pm 9.6\text{g/m}^2$ ), a thickness of  $4.2 \pm 0.5$  mils ( $106.7 \pm 12.7 \mu\text{m}$ ), a tensile strength (in the machine direction) of 31 psi (213 kPa) and (in cross direction) of 10 psi (69 kPa) and a Frazier air permeability of 6 cuft/min/sq. ft. @ 0.5 inches of water ( $182 \text{ cm}^3/\text{min}/\text{cm}^2$  @ 125 Pa).

#### THE POROUS SUPPORT LAYER

55 The porous support layer of this invention is preferably formed of a sheet or membrane of polysulfone polymer, polyvinylidene fluoride, a teflon polyfluoroethylene polymer, or more preferably of polyacrylonitrile. Typically the support layer may be of thickness of 40-80 microns, say 50 microns and of molecular weight

$\bar{M}_n$  of 5,000-100,000, preferably 20,000-60,000 say 40,000. The polyacrylonitrile is preferably characterized by a pore size of less than about 500A and typically about 200A. This corresponds to a molecular weight cut-off of less than about 100,000 typically about 20,000.

The separating layer which permits attainment of the separation in accordance with this invention may include a non-porous film of cross-linked poly(vinyl pyridine) of thickness of 1 - 10 microns, preferably 1 - 5 microns, say 3 microns. The layer is formed preferably by casting from a poly(4-vinyl pyridine) - typically the Reilline 4200 brand (of Reilly Tar and Chemical Co) of poly-4-vinyl pyridine in a 10 w% solution in a suitable solvent such as an alcohol, typical methanol.

The membrane may be formed by mixing 0.5 - 2 parts, say 1 part of the 10% - 30%, say 20 w% solution of poly(4-vinyl pyridine) in methanol with 1 part methanol, and 0.1 - 0.8 parts, say 0.52 parts, parts of aliphatic polyhalide cross-linking agent.

It is a feature of this invention that the separating layer may be a homopolymer or a copolymer of 2-vinyl pyridine or 4-vinyl pyridine. When copolymers are employed, the unit of the copolymer added to the vinyl pyridine unit may be typically vinyl chloride, ethylene, vinyl acetate, styrene, vinyl alcohol, acrylonitrile or ethylene oxide, etc.

In the preferred embodiment, the separating layer is a homopolymer of 4-vinyl pyridine of molecular weight  $\bar{M}_n$  of 10,000 - 500,000, preferably 100,000 - 300,000, say about 200,000.

The polymer may be cross-linked with a cross-linking agent to form the membranes useful in practice of this invention.

Typically the cross-linking agents may contain an aliphatic moiety, preferably containing 2 - 12 carbon atoms, typically 3 - 6 carbon atoms, say 4 carbon atoms. Although the cross-linking agent may be a polyhalide, it typically contains 2 - 5 halogen atoms, most preferably 2. The halogen is preferably bromine or less preferably chlorine or iodine. The halides may preferably be alpha, omega dihalides of linear straight chain aliphatic hydrocarbon. Typical cross-linking agents may be as tabulated below, the first listed being preferred:

#### TABLE

1,4-dibromo-n-butane (DBB)
1,5-dibromo-n-pentane (DBP)
1,10-dibromo-decane
1,4-dichloro-n-butane
1,3-dibromo-n-pentane
1,6-dibromo-n-hexane
1,8-dibromo-octane

In situ cross-linking may be carried out by casting onto the preferred polyacrylonitrile support the poly(4-vinyl pyridine) typically in the 10 w% solution in methanol to which is added the cross-linking agent (typically 1,4-dibromobutane) in mole ratio of cross-linking agent to polymer repeat unit of 0.2 - 2, say about 1.13.

It may be possible in one embodiment to cross-link the poly(4-vinyl pyridine) separating layer in one step by casting the solution of poly(4-vinyl pyridine) and polyhalide

In another embodiment, it may be possible to apply to the porous support layer, a solution of poly(4-vinyl pyridine) in an alcohol solvent. This may be dried at 40°C - 80°C, say 50°C for 2-10 minutes, say 4 minutes to form a film. The polyvinyl pyridine may then be cross-linked by soaking the film in an alcohol solution containing 1 - 50%, say 10% of a polyhalide cross-linking agent.

The composite membrane, whether prepared by the one-step or the two-step process may then be cured in an oven at 100°C-200°C, say 125°C for 1-30 minutes, say 2 minutes to yield a polyvinyl alcohol film having a thickness of 1-10 microns, say 4 microns.

## THE COMPOSITE MEMBRANE

It is a feature of this invention that the composite membrane of this invention may comprise (i) an optional carrier layer, characterized by porosity and mechanical strength, for supporting a porous support layer and a separating layer, (ii) a porous support layer of preferably polyacrylonitrile of molecular weight of 5,000 - 100,000, of thickness of 10 - 80 microns, and of molecular weight  $\bar{M}_n$  cut off of 20,000 - 200,000 and (iii) as a non-porous separating layer poly(vinyl pyridine) of molecular weight of 20,000 - 400,000 which has been cross-linked with an aliphatic polyhalide.

The composite membranes of this invention may be utilized in various configurations. It is, for example, possible to utilize the composite in a plate-and-frame configuration in which separating layers may be mounted on the porous support layer with the carrier layer.

It is possible to utilize a spiral mound module which includes a non-porous separating layer membrane mounted on a porous support layer and a carrier layer, the assembly being typically folded and bonded or sealed along all the edges but an open edge - to form a bag-like unit which preferably has the separating layer on the outside. A cloth spacer, serving as the permeate or discharge channel is placed within the bag-like unit. The discharge channel projects from the open end of the unit.

There is then placed on one face of the bag-like unit, adjacent to the separating layer, and coterminous therewith, a feed channel sheet - typically formed of a plastic net.

The so-formed assembly is wrapped around a preferably cylindrical conduit which bears a plurality of perforations in the wall - preferably in a linear array which is as long as the width of the bag-like unit. The projecting portion of the discharge channel of the bag-like unit is placed over the perforations of the conduit; and the bag-like unit is wrapped around the conduit to form a spiral wound configuration.

It will be apparent that, although only one feed channel is present, the single feed channel in the wound assembly will be adjacent to two faces of the membrane layer. The spiral wound configuration may be formed by wrapping the assembly around the conduit a plurality of times to form a readily handleable unit. The unit is fitted within a shell (in manner comparable to a shell-and-tube heat exchanger) provided with an inlet at one end and an outlet at the other. A baffle-like seal between the inner surface of the shell and the outer surface of the spiral-wound input prevents fluid from bypassing the operative membrane system and insures that fluid enters the system principally at one end. The permeate passes from the feed channel, into contact with the separating layer and thence therethrough, into the permeate channel and thence therealong to and through the perforations in the conduit through which it is withdrawn as net permeate.

In use of the spiral wound membrane, charge liquid is permitted to pass through the plastic net which serves as a feed channel and thence into contact with the non-porous separating membranes. The liquid which does not pass through the membranes is withdrawn as retentate. The liquid or vapor which permeates the membrane passes into the volume occupied by the permeate spacer and through this permeate channel to the perforations in the cylindrical conduit through which it is withdrawn from the system. In this embodiment, it will be apparent that the system may not include a carrier layer.

In another embodiment, it is possible to utilize the system of this invention as a tubular or hollow fibre. In this embodiment, the porous support layer of e.g. polyacrylonitrile may be extruded as a fine tube with a wall thickness of typically 0.001-0.1mm. The extruded tubes are passed through a bath of poly(vinyl pyridine) which is cross-linked and cured in situ. A bundle of these tubes is secured (with an epoxy adhesive) at each end in a header; and the fibres are cut so that they are flush with the ends of the header. This tube bundle is mounted within a shell in a typical shell-and-tube assembly.

In operation, the charge liquid is admitted to the tube side and passes through the inside of the tubes and exits as retentate. During passage through the tubes, permeate passes through the non-porous separating layer and permeate is collected in the shell side.

In this embodiment, it will be apparent that the system may not normally include a carrier layer. In still another embodiment, the porous support layer may be omitted; and the separating layer is extruded and thereafter cross-linked and cured in situ prior to mounting in the headers.

## PERVAPORATION

It is a feature of the non-porous separating layer that it is found to be particularly effective when used in a pervaporation process. In pervaporation, a charge liquid containing a more permeable and a less permeable component is maintained in contact with a non-porous separating layer; and a pressure drop is maintained across that layer. The charge liquid dissolves into the membrane and diffuses therethrough. The permeate which passes through the membrane and exits as a vapor may be recovered by condensing at low temperature or alternatively may be swept away by use of a moving stream of gas. Preferably, the

permeate side of the membrane is maintained at a low pressure, typically 5 mm. Hg.

For general background on pervaporation, note US 4,277,344; US 4,039,440; US 3,926,798; US 3,950,247; US 4,035,291; etc.

It is a feature of this invention that the novel membrane may be particularly useful in pervaporation processes for concentrating a charge solution containing (i) an alcohol and (ii) oxygenate selected from the group consisting of organic ethers, aldehydes, ketones, and esters.

The oxygenate may be (i) an organic ether such as dimethyl ether, diethyl ether, di-n-propyl ether, di-n-butyl ether, methyl t-butyl ether, ethyl t-butyl ether, methyl t-amyl ether, ethyl t-amyl ether;

(ii) an aldehyde such as acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde;

(iii) a ketone such as acetone, methyl ethyl ketone, diethyl ketone; or

(iv) an ester such as methyl acetate, methyl propionate, methyl butyrate, methyl benzoate, dimethyl carbonate, diethyl carbonate.

The alcohol may typically be methanol or ethanol.

It will be obvious to those skilled in the art that the process of this invention may find particular use when the charge mixture to be treated is a reaction product wherein one of the components to be separated is unreacted charge component. A typical such charge mixture is that attained from the reaction of methanol and carbon monoxide wherein the mixture may contain unreacted methanol and product dimethyl carbonate (DMC). Another illustrative charge mixture is that attained from the reaction of methanol and isobutene wherein the reaction mixture may contain methanol and methyl t-butyl ether (MTBE).

These charge solutions may have been subjected to preliminary separation, e.g. distillation, to yield, for example, an azeotrope of methanol and dimethyl carbonate.

Other charge solutions may include (i) methyl acetate-methanol, and (ii) ethyl acetate-ethanol.

In practice of the pervaporation process of this invention, the charge solution typically at 40°C-120°C, say 70°C may be passed into contact with the non-porous separating layer of the membrane of this invention. A pressure drop of about one atmosphere is commonly maintained across the membrane. Typically, the feed or charge side of the membrane is at about atmospheric pressure and the permeate or discharge side of the membrane is at a pressure of 0.5-50 preferably 5-20, say 1.5 mm.Hg, or lower.

The permeate which passes through the membrane typically includes e.g. methanol and a small proportion of the oxygenate from the charge liquid. Typically, the permeate contains 90-99 w%, say up to 99 w% methanol. Permeate is recovered in vapor phase.

Pervaporation may typically be carried out at a flux of 0.1 - 5, say about 3 kilograms per square meter per hour ( $\text{kg m}^{-2}\text{h}^{-1}$ ). Typically, the units may have a selectivity (measured in terms of w% of e.g. methanol in the permeate

during pervaporation at 70°C of a ca 30 w% solution of oxygenate through a standard polyvinyl pyridine separating layer of 3 microns thickness) of 90 - 99.9 w% methanol. It will vary depending on the oxygenate. Practice of the process of this invention will be apparent from inspection of the following non-limiting examples wherein, as elsewhere in this specification, all parts are parts by weight unless otherwise stated.

## DESCRIPTION OF SPECIFIC EMBODIMENTS

### EXAMPLE 1

In this example

the selective separating layer is mounted on the porous support layer of a commercially available (under the trademark DUY-L, from Daicel Corp) composite containing a woven polyester backing as carrier layer, bearing as porous support layer, a microporous polyacrylonitrile layer of molecular weight cut-off of 40,000.

The separating layer is formed by applying to the porous support layer, a 10w% solution in methanol of the Reilline 4200 brand (available from Reilly Company) of poly(4-vinyl pyridine) containing 20w% of 1,4-dibromobutane. Mole ratio of cross-linking agent to polymer is 1.13. The coated support is placed in an oven at 125°C for 2 minutes to dry and cure the film.

The membrane made by this method is evaluated in a pervaporation cell to which the charge is admitted at 60°C. Permeate pressure is  $1.1 \times 10^3 \text{ Nm}^{-2}$  (8 torr) at liquid nitrogen temperature.

In this preferred embodiment, the charge solution is a solution containing 31.7w% dimethyl carbonate (DMC) and 68.3w% methanol. The permeate flux is  $3.82 \text{ kg m}^{-2} \text{ h}^{-1}$  and contained 4.7w% DMC which represents a Separation Factor of 10. This flux is over three times greater than the best flux obtained in US-A-4,798,674 and the Separation Factor is higher.

EXAMPLES II - VIII

In this series of Examples, the procedure of Example I is followed except:

- (i) In Examples II and VI, the mole ratio MR of cross-linking agent to polymer is 0.86;
- (ii) In Examples IV and VII, the mole ratio MR of cross-linking agent to polymer is 1.39;
- (iii) In Examples V and VIII, the cross-linking agent is 1,5-dibromopentane and the mole ratio MR of cross-linking agent to polymer is 0.81;
- (iv) In Examples II-V, the charge contain 29.7w% of DMC and 70.3w% of methanol;
- (v) In Examples II-V, the feed temperature is 50°C.

The following Table sets forth the mole ratio (MR) of cross-linking agent to polymer; the feed concentration w% DMC; the permeate concentration w% DMC; the Flux in kilograms per square meter per hour ( $\text{kg m}^{-2} \text{h}^{-1}$ ); and the Separation Factor Sep.

TABLE

- Support: Daicel DUY-L polyacrylonitrile
- Reilline 4200, ca 20w% poly(4-vinyl pyridine)  
solids in MeOH
- Coating:  $7.6 \times 10^{-5} \text{m}$  (3 mil)

<u>Example</u>	<u>MR</u>	<u>FD CNC</u> <u>%</u>	<u>PM CNC</u> <u>%</u>	<u>FLUX</u>	<u>SEP</u>
I	1.13	31.7	4.7	3.82	9.4
II	0.86	29.7	6.5	2.83	6.1
III	1.13	29.7	5.2	2.63	7.7
IV	1.39	29.7	4.5	2.06	9.0
V	0.81	29.7	3.8	1.44	10.7
VI	0.86	31.7	6.2	4.67	7.0
VII	1.13	31.7	4.2	3.49	10.6
VIII	0.8	31.7	3.7	2.82	12.1

From the above Table, it is apparent that it is possible to attain permeate containing as little as 4.7w% DMC when charging a solution containing 31.7w% DMC - this being attained at a Flux of  $3.82 \text{ kg m}^{-2} \text{h}^{-1}$ .



EXAMPLES IX - XVII

In this series of Examples, the procedure of Example I is followed except:

- (i) In these Examples, the poly(4-vinyl pyridine) used was the Reilline 4200 brand, in concentration of 20w% solids in methanol, which was diluted with methanol to yield a 10w% stock solution;
- (ii) the mole ratio MR in Examples IX, XII, and XV is 0.86; and in Examples XI, XIV, and XVII; it is 1.39;
- (iii) the feed in Examples IX - XI contains 12.2w% methanol, 67.9w% C<sub>5</sub> hydrocarbons, and 19.8w% methyl t-butyl ether (MTBE), in Examples XII - XIV, 8.2w% methanol, 71.7w% C<sub>5</sub> hydrocarbons, and 20.1w% MTBE and in Examples XV - XVII, 8.0w% methanol, 70.5w% C<sub>5</sub> hydrocarbons, and 21.5w% MTBE;
- (iv) Separation Temperature is 35 °C in Examples IX - XIV and 45 °C in Examples XV - XVII.

TABLE

- Support: Daicel DUY-L polyacrylonitrile
- Reilline 4200 brand of polymer, ca 20% poly(4-vinyl pyridine) PVP solids in MeOH
- Coating:  $7.6 \times 10^{-5}$  m (3 mil)
- 10w% PVP in MeOH used as stock solution
- Cure conditions: 125°C/2 min

<u>Example</u>	<u>MR</u>	<u>Feed W%</u>			<u>Permeate W%</u>			<u>Flux</u>	<u>Sep</u>
		<u>MeOH</u>	<u>C<sub>5</sub></u>	<u>MTBE</u>	<u>MeOH</u>	<u>C<sub>5</sub></u>	<u>MTBE</u>		
IX	0.86	12.2	67.9	19.8	76.4	18.4	5.2	1.58	23.3
X	1.13	12.2	67.9	19.8	98.4	1.4	0.3	2.06	442
XI	1.39	12.2	67.9	19.8	97.9	1.7	0.4	1.85	336
XII	0.86	8.2	71.7	20.1	63.6	28.2	8.3	0.65	19.6
XIII	1.13	8.2	71.7	20.1	97.9	1.8	0.3	1.47	552
XIV	1.39	8.2	71.7	20.1	93.3	5.1	1.6	1.10	156
XV	0.86	8.0	70.5	21.5	67.7	23.9	8.4	0.65	24.1
XVI	1.13	8.0	70.5	21.5	96.8	2.5	0.6	1.59	348
XVII	1.39	8.0	70.5	21.5	91.8	6.4	1.8	1.21	129

From the above Table, the following conclusions may be drawn:

- (i) It is possible to treat a charge containing as much as 12.2w% methanol and obtain a permeate containing as much as 98.4w% methanol;
- (ii) it is possible to treat a charge containing as much as 67.9w% C<sub>5</sub> hydrocarbons and 19.8w% MTBE and obtain a permeate containing as little as 1.4w% C<sub>5</sub> hydrocarbons and 0.3w% MTBE;
- (iii) it is possible to obtain separation of this magnitude at a flux as high as 2.06 kg m<sup>-2</sup> h<sup>-1</sup>.

## Claims

1. A method of concentrating a charge solution containing (i) an alcohol having less than three carbon atoms and (ii) an organic oxygenate selected from organic ethers, aldehydes, ketones, esters, and mixtures thereof which comprises:  
 5       passing the charge solution into contact with a first (high pressure) side of a non-porous separating layer, a pressure drop being maintained across said layer, whereby at least a portion of said alcohol and a lesser portion of organic oxygenate from said charge solution pass by pervaporation through said non-porous separating layer to a second (low pressure) side thereof thereby providing a permeate on  
 10       the low pressure side comprising a lean mixture containing more alcohol and less organic oxygenate than are present in said charge solution, said lean mixture being recovered in vapor phase at a pressure below the vapor pressure thereof; and a retentate on the high pressure side comprising a lower alcohol content and a higher organic oxygenate content than are present in said charge solution, characterised in that said non-porous layer is a membrane of a poly(vinyl pyridine), cross-linked with an  
 15       aliphatic polyhalide.
2. A method as claimed in Claim 1 wherein said non-porous separating layer is a homopolymer of 4-vinyl pyridine which has been cross-linked with an aliphatic polyhalide.
- 20   3. A method as claimed in Claim 1 wherein said non-porous separating layer is a homopolymer of 4-vinyl pyridine of molecular weight  $\overline{M}_v$  of 100,000 - 300,000, which has been cross-linked with an aliphatic polyhalide.
- 25   4. A method as claimed in Claim 1 wherein said non-porous separating layer is a copolymer of 4-vinyl pyridine and an ethylenically unsaturated monomer, which has been cross-linked with an aliphatic polyhalide.
5. A method as claimed in any one of Claims 1 to 4 wherein said non-porous separating layer is cross-linked with an aliphatic dihalide.
- 30   6. A method as claimed in any one of Claims 1 to 5 wherein said non-porous separating layer is cross-linked with a dibromobutane.
7. A method as claimed in any one of Claims 1 to 6 wherein said separating layer has a thickness of  
 35       about 1-10 microns.
8. A method as claimed in any one of Claims 1 to 7 wherein said poly(vinyl pyridine) which has been cross-linked is supported on a porous support layer.
- 40   9. A method as claimed in Claim 8 wherein said porous support layer is a polyacrylonitrile polymer.
10. A method as claimed in any one of Claims 1 to 9 wherein said organic oxygenate is methyl t-butyl ether or dimethyl carbonate.
- 45   11. The use of a membrane comprising poly(vinyl pyridine) which has been cross-linked with an aliphatic polyhalide in concentrating a charge solution containing (i) an alcohol having less than three carbon atoms and (ii) an organic oxygenate selected from organic ethers, aldehydes, ketones, esters, and mixtures thereof.



European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 92 30 7691

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
E	US-A-5 152 898 (BARTELS) 6 October 1992 * the whole document * ---	1-11	B01D61/36 C07C29/76 C07C68/08 C07C41/36 C07C45/78
A	EP-A-0 331 846 (TEXACO) * page 5, line 15 - line 38 * * page 10, line 31 - page 11, line 20 * * claims 1,5,6; example I * ---	1,10,11	
D	& US-A-4 798 674 (PASTERNAK) ---		
D,A	EP-A-0 425 108 (TEXACO) * page 4, line 14 - line 32 * * page 6, line 50 - page 8, line 4 * * claims; examples 1,68 * ---	1-9,11	
A	EP-A-0 372 683 (TEXACO) * page 4, line 12 - line 24 * * page 7, line 42 - page 8, line 39 * * claim 1; example I * ---	1,11	
D,A	EP-A-0 480 599 (TEXACO) * claims * ---	1-9,11	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 774 365 (CHEN) * claims 1,3; example 1 * * column 4, line 43 - column 5, line 39 * -----	1,10,11	B01D C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 MAY 1993	Examiner HOORNAERT P.G.R.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

